

Macroporous styrene-divinylbenzene copolymers as carriers for poly(vinyl amine)-cobalt phthalocyanine oxidation catalysts

Citation for published version (APA):

Schutten, J. H., Hastenberg, van, C. H., Piet, P., & German, A. L. (1980). Macroporous styrene-divinylbenzene copolymers as carriers for poly(vinyl amine)-cobalt phthalocyanine oxidation catalysts. *Angewandte Makromolekulare Chemie*, 89(1), 201-219. <https://doi.org/10.1002/apmc.1980.050890117>

DOI:

[10.1002/apmc.1980.050890117](https://doi.org/10.1002/apmc.1980.050890117)

Document status and date:

Published: 01/01/1980

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Laboratory of Inorganic Chemistry and Catalysis, and Laboratory of Polymer Chemistry, Eindhoven University of Technology, P. O. Box 513, 5600 MB Eindhoven, The Netherlands

Macroporous Styrene-Divinylbenzene Copolymers as Carriers for Poly(vinylamine)-Cobaltphthalocyanine Oxidation Catalysts

Jan H. Schutten, Christianus H. van Hastenberg, Pieter Piet, and Anton L. German

(Received 17 December 1979)

SUMMARY:

Macroporous highly crosslinked styrene(St)-divinylbenzene(DVB) copolymers were prepared by solution and suspension polymerization techniques. The obtained materials allowed the grafting of poly(N-vinyl-tert-butylcarbamate) (PVCa) either by addition of VCa macroradicals to the solid bound double bonds or by termination involving the reaction of VCa macroradicals with radicals present on the carrier. Poly(vinylamine) (PVAm) grafted on St-DVB carriers was obtained after the hydrolysis of grafted PVCa with HCl and the subsequent removal of the amine-bonded HCl by means of NaOH. Heterogeneous bifunctional catalysts were obtained by attachment of cobalt(II) 4,4',4'',4'''-tetracarboxyphthalocyanine (CoPc(COOH)₄) to the grafted PVAm. The prepared catalysts were applied to the autoxidation of thiols to disulfides, both in predominantly apolar media and in aqueous media. It was demonstrated, that important prerequisites for the applicability of macroporous St-DVB copolymers as carriers for the PVAm-CoPc(COOH)₄ catalyst include a high surface area, a sufficiently large average pore diameter and accessibility of the pendent double bonds.

ZUSAMMENFASSUNG:

Makroporöse hochvernetzte Copolymere aus Styrol (St) und Divinylbenzol (DVB) wurden durch Lösungs- und Perlpolymerisation hergestellt. Die dargestellten Träger ermöglichten die Pfropfung von Poly(N-vinyl-tert-butylcarbamate) (PVCa) entweder durch Addition von VCa-Makroradikalen an die am unlöslichen Träger anhängenden Doppelbindungen oder durch Termination von VCa-Makroradikalen mit Radikalen, die sich an der Trägeroberfläche befinden. Poly(vinylamin) (PVAm) gepfropft auf St-DVB Träger wurde durch Hydrolyse von gepfropftem PVCa mit HCl und nachfolgende Entfernung von amingebundenem HCl mittels NaOH erhalten. Heterogene bifunktionelle Katalysatoren wurden dargestellt durch Bindung von Kobalt(II) 4,4',4'',4'''-tetracarboxyphthalocyanin (CoPc(COOH)₄) an gepfropftes PVAm. Die

hergestellten Katalysatoren wurden zur Oxidation von Thiolen zu Disulfiden, sowohl in vorwiegend apolaren als auch in wäßrigen Lösungsmitteln verwendet. Es wurde bewiesen, daß eine große innere Oberfläche, ein hinreichend großer mittlerer Porendurchmesser und Zugänglichkeit der anhängenden Doppelbindungen wichtige Voraussetzungen sind für die Anwendbarkeit vom makroporösen St-DVB Copolymeren als Träger für den PVAm-CoPc(COOH)₄ Katalysator.

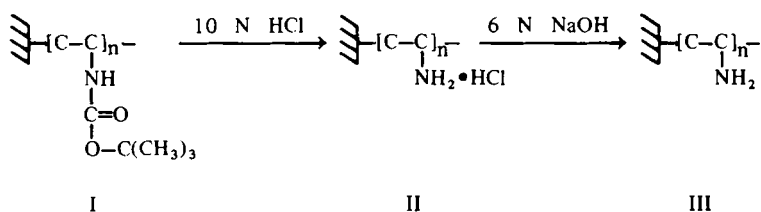
Introduction

Catalysis by complexes of transition metals anchored on macromolecular ligands currently receives considerable attention^{1,2}. Many polymer-metal complexes show a high catalytic efficiency because the polymer chains create a favourable micro-environment for the catalytic sites. Recently^{3,4,5}, we reported on a bifunctional catalyst for the autoxidation of thiols composed of a cobaltphthalocyanine (CoPc) and poly(vinylamine) (PVAm). The remarkable high activity of this catalyst could be explained by taking into account phenomena inherently connected with the polymeric character of PVAm.

A disadvantage limiting the practical applicability of the PVAm-CoPc catalyst is its solubility in the reaction medium preferentially applied (i. e. water), as the separation of the catalyst from the reaction product and the catalyst regeneration are difficult to achieve. Therefore, the idea appeared that the advantages might be retained and the disadvantages overcome if the PVAm-CoPc catalyst was chemically bound onto a solid carrier. This immobilization should be carried out in such a way that the polymeric character of PVAm, which is an essential requirement for a high catalytic activity⁵, will be maintained. Macroporous copolymers of styrene (St) and commercial divinylbenzene (DVB) were used as carriers in this investigation. St-DVB copolymers may be prepared as spherical beads with a variety of particle size distributions (using suspension polymerization techniques), which strongly enhances the applicability of this class of supports in technical reactors. St-DVB copolymers are being widely applied in the preparation of ion exchangers and as beads for analytical purposes (gel permeation chromatography and gas liquid chromatography)^{6,7}. More recently, this class of copolymers, which possesses good mechanical and chemical stability, has also been applied as carrier for homogeneous catalysts¹.

Macroporous polymer networks are heterogeneously crosslinked polymers, which may be obtained when high amounts of crosslinking agent are

used and the monomers are diluted with an inert compound^{6,7}. During the preparation of these copolymers part of the divinylbenzene monomers are incorporated into the network with a single vinyl group only^{8,9}. So the resulting material will contain a certain amount of unreacted or pendent double bonds. When vinyl monomers are polymerized in the presence of these reactive carriers graft copolymers may be obtained¹⁰. The present paper describes the grafting of N-vinyl-tert-butylcarbamate onto St-DVB copolymers. The aim of the investigation was the preparation of poly(vinylamine) grafted onto a St-DVB carrier (III), by the hydrolysis of grafted poly(N-vinyl-tert-butylcarbamate) (I) and the subsequent removal of the amine-bonded hydrogen chloride (see scheme 1). After coupling CoPc to the grafted PVAm (III) a heterogeneous bifunctional catalyst should be obtained, which may be expected to show activity in the autoxidation of thiols to disulfides.



Scheme 1. Preparation of grafted poly(vinylamine) from grafted poly (N-vinyl-tert-butylcarbamate).

Experimental

Instrumentation

A Hewlett Packard (Model 185) apparatus was used for C, H, N analysis. Co-contents were determined by means of neutron activation analysis using a Ge(Li)-semiconductor detector. IR spectra were recorded on a Hitachi EPI G spectrophotometer. Surface areas were determined with a Ströhlein Areameter. Scanning Electron Microscopy was carried out with a Stereoscan Mark 2A apparatus (Cambridge Scientific Instruments Ltd.). Number average molecular weights were determined with a Hewlett Packard High Speed Membrane Osmometer 502 (solvent: toluene, T = 37°C). A Hewlett Packard gas chromatograph 5700 A equipped with a flame ionization detector and a Hewlett Packard integrator 3380 A were used. A stainless

steel column (3.8 m × 2 mm, i. d.) has been applied packed with 20% Silicone oil DC 550 on Chromosorb P (60/80 mesh), operated with a helium flow rate of 30 ml min⁻¹.

Reagents

Styrene (Merck) and commercial divinylbenzene (Merck) were washed with 2 N NaOH, neutralized, dried over CaH₂ and distilled in vacuo. GLC analysis of inhibitor-free commercial divinylbenzene gave the following results: 33.6 wt.-% m-ethylvinylbenzene, 11.2 wt.-% p-ethylvinylbenzene, 39.3 wt.-% m-divinylbenzene, 14.1 wt.-% p-divinylbenzene and some very small amounts of m- and p-diethylbenzenes and naphthalene (see also^{11,12}). N-vinyl-tert-butylcarbamate (VCa) was prepared from acryloylchloride on the analogy of the method given by Hughes et al.¹³; m.p. 65.5--66.5°C, Lit.¹³ 67--68°C. 2,2'-Azobisisobutyronitrile (AIBN) (Merck) was purified by recrystallization from diethylether.

Preparation of Macroporous Styrene-Divinylbenzene Carriers^{6,7,14,15}

a) Polymers of inhibitor-free commercial divinylbenzene (3.0 g) were prepared by solution polymerization in the presence of 6.0 ml diluents (mixtures of toluene and n-butanol) with AIBN as initiator. The reactions were carried out in sealed ampoules (under nitrogen) at 80°C in a thermostated water bath, the reaction time was 8 h. The materials obtained were powdered, extracted with cyclohexane in a soxhlet-apparatus and subsequently dried in vacuo.

b) Polymers of purified commercial divinylbenzene (27.0 g) and styrene (3.0 g) were prepared by suspension polymerization in the presence of 60 ml diluent with 300 mg AIBN as initiator. The reaction was carried out in 250 ml water with 4 g/l polyvinyl alcohol (Koch-Light Laboratories Ltd., $M_n \approx 72\ 000$) as suspension agent, reaction time 6 h at 80°C. The polymerizations were run in a standard suspension polymerization apparatus (SFS) consisting of a 1 litre, double-walled, round-bottomed cylindrical flask fitted with a mechanical stirrer and nitrogen in- and outlet tubes. Before starting the polymerization nitrogen was flushed through the solution during 15 min, the stirring speed was 550 r. p. m. The reaction was stopped by the addition of p-tert-butylpyrocatechol. Steam distillation was used to remove unreacted monomers and the solvent-non solvent mixture. The distillate was collected during 2 h in a flask containing some inhibitor. Then, the organic layer was separated and the aqueous part of distillate was extracted twice with 50 ml n-hexane. The amounts of unreacted monomers in the collected organic extraction liquids were determined by GLC with α -methylstyrene as an internal reference. The obtained polymer beads were washed and dried, and the size distribution was determined by sieve analysis. IR-spectra of all carriers were recorded from KBr-pellets (1 wt.-% of polymer) and also from a nujol suspension using finely powdered polymer with particle size < 20 μm^9 (75 mg of polymer in 0.5 ml nujol, thickness 1 mm).

Grafting of Poly(N-vinyl-tert-butylcarbamate) (PVCa) onto the Macroporous Styrene-Divinylbenzene Copolymers

A typical grafting experiment was performed in the following way. In a sealed ampoule N-vinyl-tert-butylcarbamate (VCa) was polymerized (under nitrogen) in the presence of a carrier containing pendent vinyl groups. The polymerization was initiated with $1.2 \cdot 10^{-2}$ mol AIBN/mol VCa, cyclohexane was used as a solvent and the reaction was performed at 50°C during 72 h. The resulting reaction mixture was diluted with acetone/cyclohexane (1 : 1, v/v). The solid product was collected and extracted with acetone (3 h) and cyclohexane (1 h), successively, in a soxhlet apparatus; finally the product was dried in vacuo. The content of grafted VCa in the materials was determined by N-analysis. The free homopolymer, PVCa, was obtained from the acetone/cyclohexane (1 : 1, v/v) solution, by precipitation with cold n-hexane.

Hydrolysis of Grafted PVCa

Grafted PVCa (I) was hydrolyzed by stirring or shaking the solid product in an ethanol/10 N hydrochloric acid (1 : 1, v/v) mixture on the analogy of methods developed earlier for the hydrolysis of free PVCa^{4, 13, 16}. This reaction was carried out during 8 h at ambient temperature. After neutralizing with ethanol/water mixtures and finally with pure ethanol, the product was dried in vacuo.

Desalting of Grafted PVAm-HCl

Removal of bonded HCl was achieved by stirring or shaking the product for 7 h at ambient temperature (under nitrogen) in a 6 N NaOH/ethanol (1 : 1, v/v) mixture. The resulting material was washed with ethanol/water mixtures and subsequently dried in vacuo.

Catalyst Preparation

Cobalt(II) 4,4',4'',4'''-tetracarboxyphthalocyanine (CoPc(COOH)₄) and its tetrasodiumsalt (CoPc(COONa)₄) were prepared as described in a previous paper⁴. Complexation of CoPc(COONa)₄ with (III) and covalent attachment of CoPc(COOH)₄ to (II) were achieved analogous to methods developed earlier⁴ in behalf of the binding of CoPc derivatives to soluble PVAm.

Catalytic Activity Measurements

Activity measurements were carried out in an all-glass, thermostated ($T = 23^{\circ}\text{C}$), double-walled Warburg apparatus provided with a mechanical (glass) stirrer. The substrate, 2-mercaptoethanol (Merck) was distilled before use and carefully kept under nitrogen. The reaction rate was determined by measuring the initial oxygen consumption rate at constant oxygen pressure ($p(\text{O}_2) = 1 \text{ atm}$) and at constant stirring speed (3000 r. p. m.).

Results and Discussion

Macroporous Styrene-Divinylbenzene Copolymers

We aimed at preparing macroporous St-DVB copolymers with optimal characteristics, such as surface area, average pore diameter and amount of pendent vinyl groups accessible to the grafting of poly(N-vinyl-tert-butyl-carbamate). The internal surface and the pore size distribution may be optimized by using a mixture of a solvent and a precipitant for the (uncross-linked) polymer during polymerization^{6,7,14}. Good solvents will produce small pores, bad solvents large pores. In this investigation, toluene was used as a solvent and n-butanol as a nonsolvent.

In Fig. 1 the surface areas of the polymers obtained from the solution polymerization of commercial DVB are shown as a function of the composition of the diluent mixture. The maximum value of the surface area occurs at the ratio n-butanol:toluene = 1:3, in agreement with the results of Heitz^{7,14}. Scanning electron microscopy reveals that the average pore diameter increases with decreasing toluene content in the inert phase. These findings are in accordance with literature^{6,7,14}. The infrared absorption spectra of the crosslinked copolymers (in nujol) show a significant peak at 1630 cm^{-1} assigned to monosubstituted vinyl groups. The characteristic absorption at 1600 cm^{-1} of the skelet vibration of the aromatic nucleus of polystyrenes was used as a reference. The ratio of the extinctions at 1630 cm^{-1} and 1600 cm^{-1} ($E_{1630 \text{ cm}^{-1}}/E_{1600 \text{ cm}^{-1}}$) then may be used as a quantitative measure of the residual double bounds⁹. The results presented in Fig. 1 reveal that the relative content of pendent vinyl groups is rather constant at high toluene contents, but increases rapidly when the inert phase contains less than 25% toluene. This phenomenon may be explained by considering the mode of network formation^{6-8,17} as a function of the composition of the inert phase. When the inert phase contains non-solvent (n-butanol) only, the

Macroporous Styrene-Divinylbenzene Copolymers as Carriers

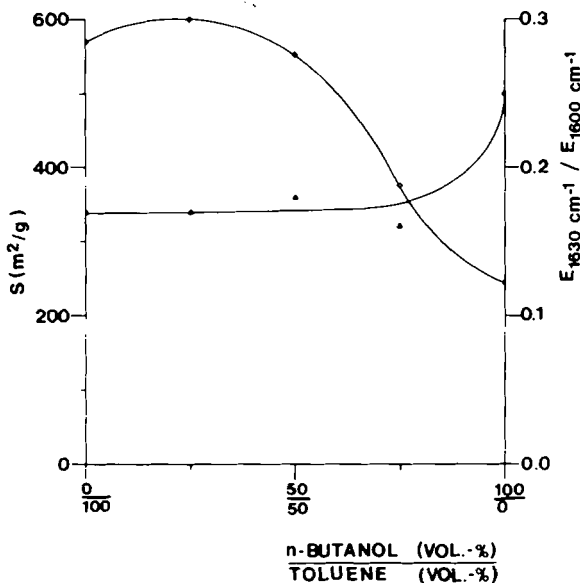


Fig. 1. Macroporous St-DVB copolymers prepared by solution polymerization. Surface areas (S) [\diamond] (measurements on particles with $d < 100 \mu\text{m}$) and residual double bonds ($E_{1630 \text{ cm}^{-1}}/E_{1600 \text{ cm}^{-1}}$) [\triangle] as a function of the composition of the inert phase during preparation.

polymer chains initially formed with pendent vinyl groups will be weakly solvated and therefore be relatively highly contracted. During further polymerization the pendent vinyl groups will remain relatively inaccessible and the resulting network will contain a comparatively large amount of double bonds. When the amount of solvent (toluene) in the inert phase is increased the polymer chains will become more solvated and thus more expanded. As a result the pendent vinyl groups will remain more accessible to addition reactions. It may be concluded that the St-DVB copolymers prepared at high n-butanol contents will contain relatively many residual double bonds, though poorly accessible.

In Fig. 2 the IR-data and the surface areas of copolymers prepared by suspension polymerization of 10 wt.-% St and 90 wt.-% commercial DVB mixtures are shown as a function of the composition of the inert phase. The results given in Fig. 1 and 2 exhibit corresponding trends in accordance with the data reported in the literature for similar cases^{7,14}.

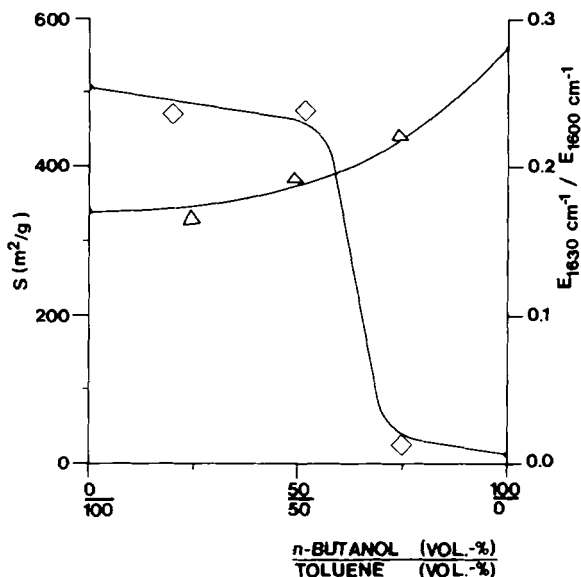


Fig. 2. Macroporous St-DVB copolymers prepared by suspension polymerization. Surface areas (S) [◇] (particle size $200 \mu\text{m} < d < 300 \mu\text{m}$) and residual double bonds ($E_{1630 \text{ cm}^{-1}}/E_{1600 \text{ cm}^{-1}}$) [△] as a function of the composition of the inert phase during preparation.

The preparation of macroporous polymers by suspension polymerization has been investigated with respect to a number of characteristic phenomena. These characteristics include a higher reactivity of DVB as compared with styrene and ethylvinylbenzenes¹², which appears from Tab. 1 and Fig. 3. It also appears that the mode of the cumulative particle size distribution curves (Fig. 4) tends to shift to higher values as the toluene content in the inert phase increases. Fig. 4 also reveals that the distributions become broader as the toluene content increases.

From scanning electron micrographs it appeared that with increasing n-butanol content the shape of the particles becomes less spherical. The latter observation is in agreement with the results of Wolf et al.¹⁵, who observed that the percentage of deformed particles increased on addition of a water-soluble alcohol to the reaction medium. As expected^{6,7,14}, the micrographs confirm that the average pore diameter increases as the n-butanol content in the inert phase increases. Simultaneously the materials become more brittle, which is in accordance with the literature data^{14,17}.

Macroporous Styrene-Divinylbenzene Copolymers as Carriers

Tab. 1. Composition of St-DVB macroporous copolymers^a prepared from a monomer mixture of 10 wt.-% St and 90 wt.-% commercial DVB^b using inert phases of varying composition.

Carrier no.	toluene n-butanol (vol.-%) ^c	St (%) ^a	m-EVB (%)	p-EVB (%)	m-DVB (%)	p-DVB (%)
6	100/0	10.14	30.59	10.14	36.15	12.97
7	75/25	10.15	30.69	10.18	36.03	12.95
8	50/50	10.11	30.67	10.21	36.04	12.97
9	25/75	9.74	30.09	9.98	36.89	13.30
10	0/100	9.34	29.51	9.56	37.81	13.78

^a Composition is given in wt.-%, the values were calculated using the results of the GLC determination of the amounts of unconverted monomers.

^b Preparation by suspension polymerization technique; composition of commercial DVB is given in the experimental part.

^c Composition of inert phase during preparation.

Grafting of Poly(N-vinyl-tert-butylcarbamate) onto Macroporous Styrene-Divinylbenzene Copolymers

a. Grafting Method

Grafting of PVCa is achieved by radical polymerization of N-vinyl-tert-butylcarbamate (VCa), initiated by AIBN, in the presence of the reactive St-DVB solid carriers. Graft copolymer is formed by chain propagation involving coupling of a growing VCa macroradical (P^*) to the solid bound double bonds (Eq. 1, scheme 2). Grafting may also occur by termination of the growing VCa macroradicals with radicals generated on the carrier (Eq. 2 and 5). On the one hand efficient grafting will require solid carriers that possess a large internal surface, a sufficiently large average pore diameter and also a sufficient amount of accessible double bonds. Macroporous St-DVB copolymers^{6-9,14,17} can meet these requirements within certain limits. On the other hand, the copolymerization kinetics will affect the grafting characteristics to a high degree. Because the copolymerization behaviour of VCa and VAc (vinylacetate) are comparable¹⁸, the grafting mechanism of

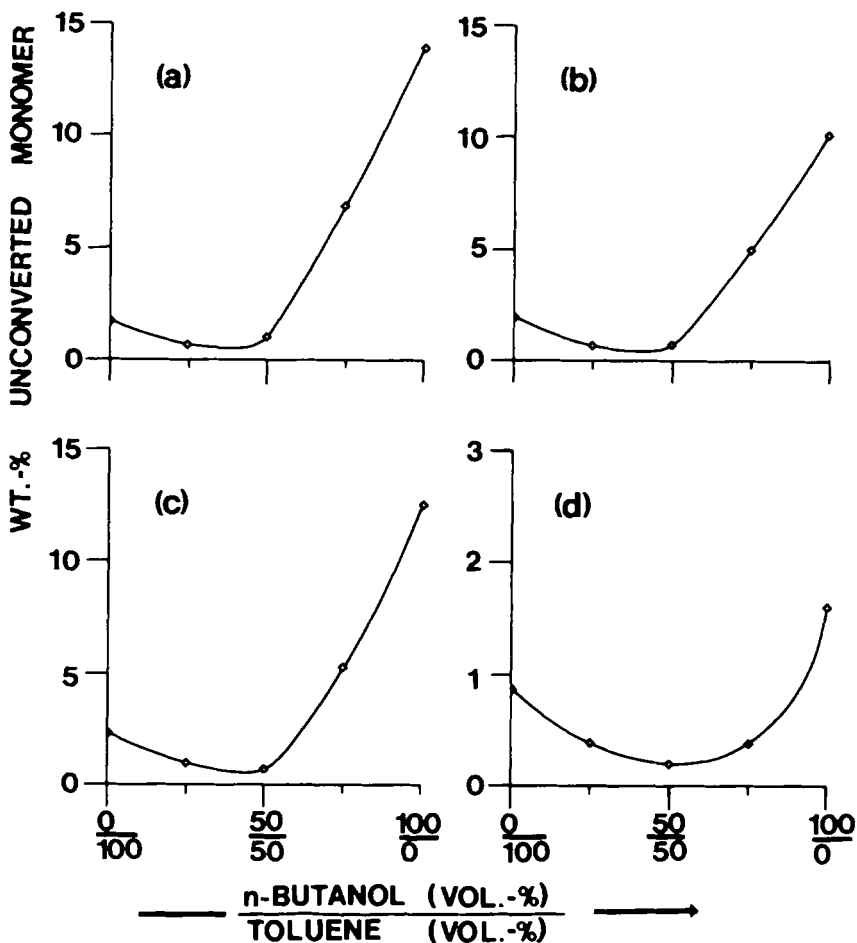


Fig. 3. Relative amount of unreacted monomer as determined by GLC analysis versus composition of the inert phase applied during the suspension polymerization of a monomer mixture initially containing 10 wt.-% St and 90 wt.-% commercial DVB (conditions: see experimental). a styrene; b m-ethylvinylbenzene; c p-ethylvinylbenzene; d m-divinylbenzene (p-divinylbenzene was totally converted).

VCA onto these St-DVB carriers may be better understood when reviewing the literature on the attempted grafting of VAc on polystyrene^{19,20}. It is well established that the copolymerization parameters of styrene (r_1) and VAc (r_2)

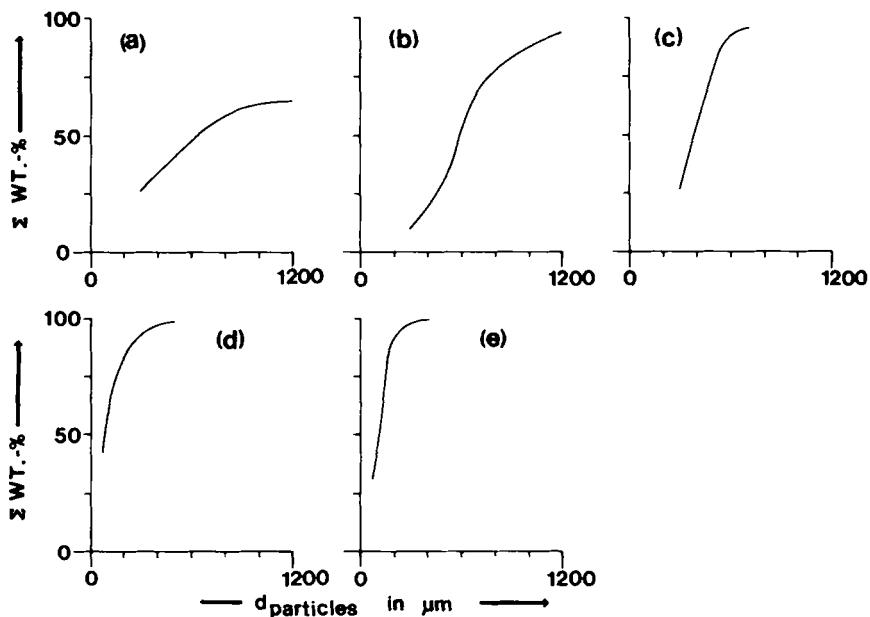
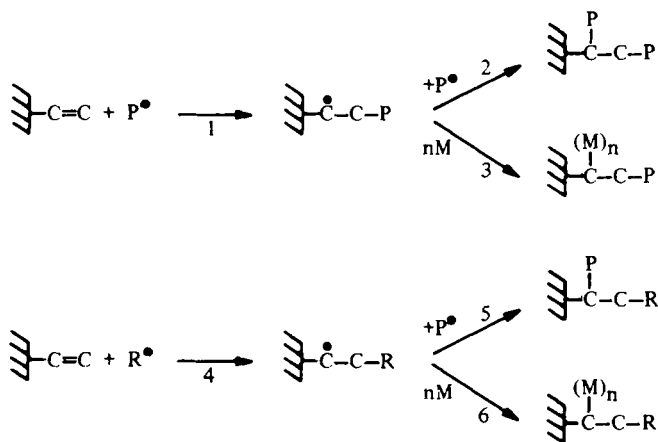


Fig. 4. Cumulative particle size distributions obtained from sieve analysis of St-DVB copolymers (prepared by suspension polymerization of 10 wt.-% St and 90 wt.-% commercial DVB). The composition of the inert phase applied during preparation was varied: a 100/0; b 75/25; c 50/50; d 25/75; e 0/100 (v/v) toluene/n-butanol.

are quite unfavourable to copolymer formation ($r_1 = 55$, $r_2 = 0.01$)²¹. This indicates that grafting initiated by a radical on the solid surface, as represented by Eq. 3 and 6, will occur only rarely because of the low relative reactivity of the VAc and VCa monomers towards an unreactive styrene-type radical. Furthermore, it has been observed that AIBN is unable to initiate grafting of for instance methyl methacrylate on polystyrene by a radical transfer mechanism because the reactivity of the resonance stabilized $(\text{CH}_3)_2\text{C}^-\text{CN}$ radical is too low²². Because of the relatively low reactivity of AIBN, it is very improbable that AIBN will initiate the graft copolymerization of VCa starting from the St-DVB carrier by a chain transfer mechanism.



Scheme 2. Grafting of VCa macroradicals (P^\bullet) on St-DVB carriers with pendent double bonds ($R = (CH_3)_2\dot{C}-CN$, $M = VCa$).

b. Results of the Grafting Experiments.

The experimental results of the grafting of PVCa onto St-DVB carriers of various composition are presented in Tab. 2. St-DVB copolymers prepared in the presence of a relatively high content of n-butanol possess the highest density of pendent vinyl groups, but nevertheless they exhibit very low percentages of grafted PVCa. Evidently, in the latter case the double bonds are not accessible to growing VCa macroradicals, as was anticipated in the preceding section.

It appears that the internal surfaces of the carriers (S) and the amount of grafting are not directly related, though it is evident that a too low internal surface should have a deleterious effect on the grafting efficiency.

In conclusion, it appears that the materials prepared in the presence of an inert phase consisting of 75 vol.-% toluene and 25 vol.-% n-butanol are the most suitable carriers for the grafting of PVCa. These carriers combine a large surface area with a sufficiently large average pore diameter, while they possess a reasonable amount of accessible pendent double bonds.

As no grafting occurred in the absence of AIBN, a radical initiator appears to be essential in order to obtain grafting. Also PVCa was allowed to react with the macroporous copolymers (50 °C, 24 h, in cyclohexane). The materials obtained, after purification, contained no detectable amounts of

Macroporous Styrene-Divinylbenzene Copolymers as Carriers

Tab. 2. Grafting of poly (N-vinyl-tert-butylcarbamate) as a function of the specific surface and the amount of residual double bonds of the St/DVB carriers.

Carrier no. ^a	$\frac{\text{toluene}}{\text{n-butanol}}$ (vol.-%) ^b	S ^c (m ² /g)	$\frac{E_{1630\text{ cm}^{-1}}}{E_{1600\text{ cm}^{-1}}}$	PVCa ^d (wt.-%)
1	100/0	569	0.17	10
2	75/25	600	0.17	12
3	50/50	552	0.18	10
4	25/75	376	0.16	11
5	0/100	244	0.25	4
6	100/0	504	0.17	13
7	75/25	477	0.17	17
8	50/50	468	0.19	9
9	25/75	35	0.22	5
10	0/100	12	0.28	4

^a Carriers 1--5 prepared from commercial DVB by solution polymerization technique, particle size $d < 100\ \mu\text{m}$; carriers 6--10 prepared from 10 wt.-% St and 90 wt.-% commercial DVB (see Tab. 1) by suspension polymerization technique, particle size $200 < d < 300\ \mu\text{m}$.

^b Composition of inert phase during preparation of carriers.

^c S = internal surface.

^d Grafting onto carriers 1--5 was carried out without stirring using 50 mg of powdered carrier, 150 mg VCa, 0.5 ml cyclohexane, 2.5 mg AIBN; grafting onto carriers 6--10 as described in the experimental part.

PVCa (i. e. $< 1.5\ \text{wt.-%}$). The latter result also proves that the extraction method applied efficiently removes the free (physically attached) PVCa from the carrier.

c. Average Block Length of the Grafted PVCa

An important prerequisite for obtaining an active catalytic system is a sufficiently large⁵ average block length of the grafted PVCa. As a first approximation the block length might be obtained from the number of grafting sites and the total amount of grafted PVCa. The number of grafting sites may be determined by IR-measurement of the number of pendent vinyl

groups⁹ before and after the grafting reaction. Application of this method provides an indication of \bar{P}_n in the grafted PVCa (I) samples investigated, i.e. $4 \leq \bar{P}_n \leq 12$. However, it has been shown experimentally that the initiator (AIBN) can also consume the pendent double bonds (Eq. 4), which does not necessarily result in an effective grafting site. Consequently, the described method leads to too low values for the average block length. The number average degree of polymerization (\bar{P}_n) of the extracted free homopolymers was found to be approximately 400 (using $1.2 \cdot 10^{-2}$ mol AIBN/mol VCa). Up to now no reliable method has been available for the determination of the average block length of the grafted PVCa.

d. IR-Characterization of the Grafted PVCa Samples.

In a mixture containing (for example) 50 wt.-% PVCa (obtained from a regular homopolymerization of VCa) and 50 wt.-% St-DVB copolymer the main IR-absorption of the NH-group (see Fig. 5a) is found at 3350 cm^{-1} (NH-group with interaction), while a distinct shoulder shows up at 3440 cm^{-1} (NH-group without interaction). In this sample the C=O absorption was found at 1700 cm^{-1} (Fig. 5b).

The IR-spectrum of grafted PVCa (St-DVB carrier 2, see Tab. 2) shows that the main absorption of the NH-groups is found at 3420 cm^{-1} (Fig. 5c), indicating the practical absence of hydrogen bonding. In the latter case the C=O adsorption (Fig. 5d) is shifted to 1715 cm^{-1} . From these shifts, it may be inferred that the grafted PVCa occurs as relatively isolated chains within the pores of the carrier. However, these phenomena should depend on the pore size of the carrier applied. Using a carrier with larger pores (St-DVB carrier 5, see Tab. 2), indeed led to a spectrum (see Fig. 5e and 5f) similar to that of a physical mixture (compare with Fig. 5a and 5b). Evidently, the larger pore size allows the grafted PVCa chains to form hydrogen bonds, and consequently the IR-spectrum shows interactions similar to those in the physical mixtures of PVCa and St-DVB copolymer.

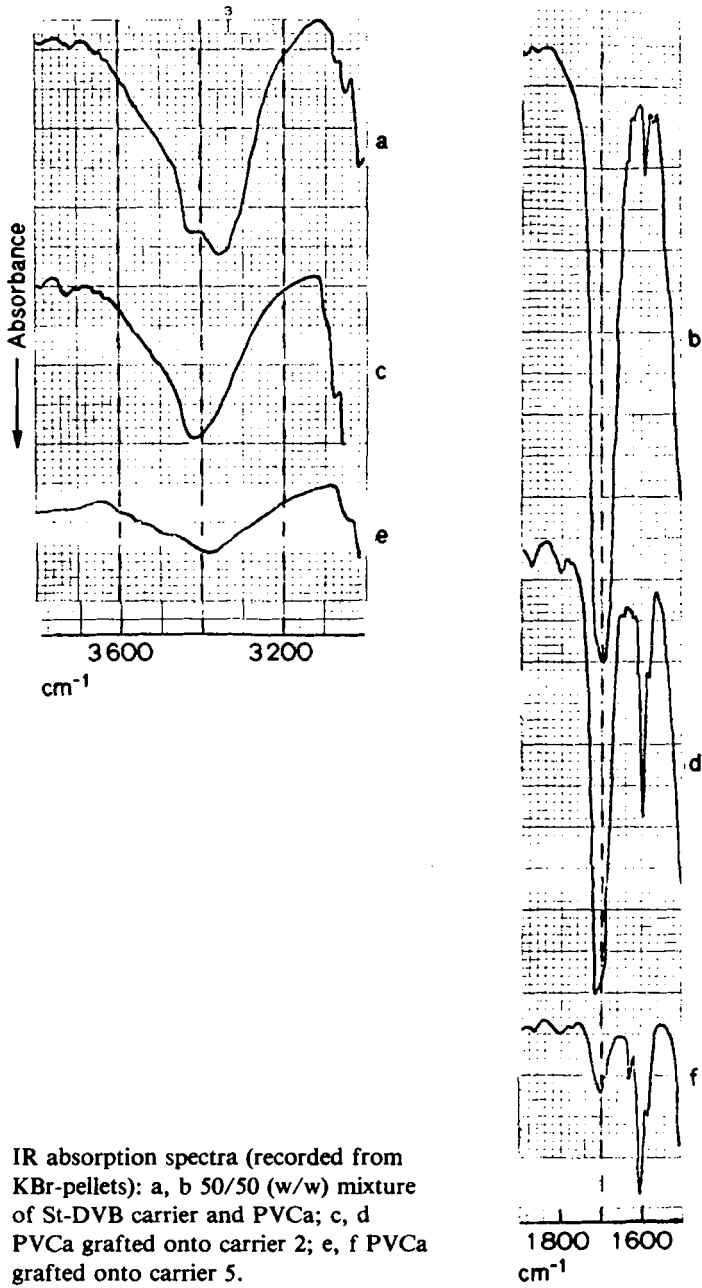


Fig. 5. IR absorption spectra (recorded from KBr-pellets): a, b 50/50 (w/w) mixture of St-DVB carrier and PVCa; c, d PVCa grafted onto carrier 2; e, f PVCa grafted onto carrier 5.

Preparation of Grafted Poly(vinylamine) from Grafted Poly(N-vinyl-tert-butylcarbamate)

Previous investigations^{4,13,16} have revealed that the hydrolysis of the homopolymer PVCa can be achieved properly using 10 N hydrochloric acid (HCl) in ethanol (1 : 1, v/v). Therefore, in this investigation the hydrolysis of grafted PVCa (I) was also carried out under these conditions (see experimental). After hydrolysis, IR spectra of the reaction products showed that the C=O absorption of the samples (spectra in nujol) had practically vanished, indicating the grafted carbamate polymer (I) was almost completely converted into the grafted hydrogen chloride salt of poly(vinylamine) (PVAm-HCl, II).

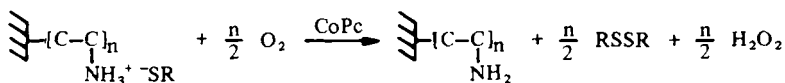
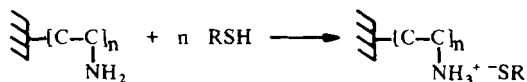
Since the PVAm-HCl is grafted onto insoluble carriers the removal of bonded HCl cannot be carried out in the usual manner (i. e., passage of an aqueous solution of PVAm-HCl through an ion-exchange column^{3,4,16}). In the present case we have resorted to a 6 N NaOH/ethanol (1 : 1, v/v) mixture for the conversion of (II) into (III). This method was proved to be effective since no chloride could be detected with AgNO₃.

A reliable proof of the versatility of the described method was obtained by hydrolyzing (I) with nitric acid (HNO₃) instead of HCl. Although HNO₃ has a strong absorption at 1380 cm⁻¹, no remaining HNO₃ was observed by IR-analysis after desalting of the HNO₃-analog of (II).

Catalytic Activities of the Heterogeneous Bifunctional Catalysts

Attachment of CoPc moieties to the grafted PVAm (III) was achieved either by complexation through the polymeric amine groups or by formation of a peptide linkage between the grafted PVAm and the phthalocyanine ring system (see experimental and cf.⁴).

The catalytic properties of the resulting heterogeneous bifunctional catalysts were tested for the autoxidation of thiols to disulfides:



Macroporous Styrene-Divinylbenzene Copolymers as Carriers

The results presented in Tab. 3 indicate that both methods of coupling CoPc to the grafted PVAm provide bifunctional catalysts, which do not require additional alkaline base to obtain high activities. Most of the heterogeneous bifunctional catalysts prepared are found to be substantially more active than the traditional catalytic systems (i. e. without polymeric base in the presence of NaOH).

Tab. 3. Catalytic activities of the polymeric catalysts for the autoxidation of 2-mercapto-ethanol^a.

Carrier no. ^b	Amine (mmol)	CoPc (μmol)	Method of coupling ^c	v (ml O ₂ μmol Co ⁻¹ min ⁻¹)	Reaction medium (ml/ml)
6	0.01	0.01	A	20	water/toluene 1/70
7	0.01	0.01	A	50	1/70
9	0.01	0.01	A	8	1/70
6	0.01	0.004	B	84	1/70
7	0.02	0.01	B	13	1/70
9	0.01	0.04	B	4	1/70
—	0.02	0.01	A	74	1/70
—	0.10	0.01	B	442	1/70
4	0.02	0.01	A	48	water/ethanol 70/7
4	0.01	0.17	B	77	70/7
—	0.02	0.01	A	300	70/7
—	— ^d	0.01	—	7	water 75
—	0.02	0.01	A	408	water 75
—	0.10	0.01	B	444	water 75

^a Reaction conditions: see Experimental, 1 ml (14.25 mmol) substrate was used in all cases.

^b St-DVB copolymer, see Tab. 2.

^c A = CoPc(COONa)₄ coupled through complexation to PVAm, time of complexation 1 h; B = CoPc(COOH)₄ covalently coupled to PVAm (see text).

^d Without polymeric base, but with 1.0 mmol NaOH.

Since the soluble as well as the immobilized polymeric catalysts require far less basic groups per cobalt site than the traditional systems to obtain even higher catalytic activities, it may be inferred that the polymeric catalytic systems are characterized by an efficient cooperation between basic sites and

oxidation sites. However, it also appears that using grafted PVAm the catalytic activity is significantly lower than when using ungrafted PVAm. It is assumed that the hydrophobic environment created by the St-DVB matrices and diffusion limitation (i. e., restricted transport of reactants to the active sites) are responsible for this phenomenon. At present, however, it cannot be excluded that too small an average block length (\bar{P}_n) of the grafted PVAm also contributes to the relatively low activities observed. When \bar{P}_n becomes too low the CoPc units will not be protected sufficiently by the PVAm chains against dimerization reactions, which causes deactivation of the catalyst^{3,5}.

The hydrophobic character of the St-DVB carriers prohibits the formation of a proper dispersion of the catalyst particles in pure water, consequently experiments in pure water have not been subjected for further investigation. Addition of ethanol to the reaction medium gave improvement of the dispersability and activity of these catalysts. In the present as well as in a previous⁴ investigation bifunctional catalysts have also shown remarkable activities in toluene provided that small amounts of water are present (see Tab. 3). Up to now, no straightforward relationship between the specific catalytic activities observed and the properties of the macroporous St-DVB carrier could be determined. However, it appears that the PVAm/CoPc catalysts immobilized on carriers with a low internal surface (i. e., large average pore diameter) exhibit a low catalytic activity (see for instance Tab. 2 and 3, carrier 9). This result fits in with the observed effect of the pore size on intermolecular interactions of grafted polymer chains (see the preceding section). When a constant [CoPc]/[amine] ratio is applied, the increased interaction between grafted PVAm chains in wide pores compared with narrow pores will cause an enhanced probability of CoPc dimerization reactions (i. e., deactivation).

Obviously a high surface area (i. e., relatively small average pore diameter) is an important prerequisite for obtaining a good catalytic activity. From the results presented in Tab. 2 it appears that efficient grafting also calls for a high surface area. On the other hand it is evident that both grafting efficiency and catalytic performance impose restrictions on the minimum pore diameter. Finally, it may be concluded that within the present series of St-DVB carriers, the most effective catalysts are obtained from those carriers allowing the highest percentage of PVAm grafting.

The authors wish to acknowledge the contributions of H. C. B. Ladan, J. P. Nelissen and L. M. C. Paulissen to the experimental work.

Macroporous Styrene-Divinylbenzene Copolymers as Carriers

- ¹ Y. Chauvin, D. Commereuc, F. Dawans, *Prog. Polym. Sci.* **5** (1977) 95
- ² E. Tsuchida, H. Nishide, *Fortschr. Hochpolym.-Forsch.* **24** (1977) 1
- ³ J. Zwart, H. C. van der Weide, N. Bröker, C. Rummens, G. C. A. Schuit, A. L. German, *J. Mol. Catalysis* **3** (1977) 151
- ⁴ J. H. Schutten, J. Zwart, *J. Mol. Catalysis* **5** (1979) 109
- ⁵ J. H. Schutten, P. Piet, A. L. German, *Makromol. Chem.* **180** (1979) 2341
- ⁶ J. Seidl, J. Malinský, K. Důšek, W. Heitz, *Fortschr. Hochpolym.-Forsch.* **5** (1967) 113
- ⁷ W. Heitz, *Fortschr. Hochpolym.-Forsch.* **23** (1977) 1
- ⁸ K. A. Kun, R. Kunin, *J. Polym. Sci., Part A-1* **6** (1968) 2689
- ⁹ J. W. Breitenbach, I. Fučík, *Monatsh. Chem.* **99** (1968) 2436
- ¹⁰ H. A. J. Battaerd, G. W. Tregear, *Graft Copolymers*, in *Polym. Rev.*, Ed. H. F. Mark, E. H. Immergut, Interscience Publishers, John Wiley, New York 1967, Vol. 16, p. 18
- ¹¹ R. E. Hannah, M. L. Cook, J. A. Blanchette, *Anal. Chem.* **39** (1967) 358
- ¹² R. H. Wiley, *Pure Appl. Chem.* **43** (1975) 57
- ¹³ A. R. Hughes, T. St. Pierre, *Macromol. Synth.* **6** (1977) 31
- ¹⁴ W. Heitz, R. Michels, *Makromol. Chem.* **148** (1971) 9
- ¹⁵ F. Wolf, S. Eckert, *Plaste. Kautsch.* **18** (1971) 725, 727
- ¹⁶ C. J. Bloys van Treslong, C. F. H. Morra, *Rec. Trav. Chim. Pays-Bas* **94** (1975) 101
- ¹⁷ J. R. Millar, D. G. Smith, T. R. E. Kressman, *J. Chem. Soc.* **1965**, 304
- ¹⁸ C. J. Bloys van Treslong, private communication
- ¹⁹ G. Smets, M. Claesen, *J. Polym. Sci.* **8** (1952) 289
- ²⁰ G. Smets, R. Hart, *Fortschr. Hochpolym.-Forsch.* **2** (1960) 173
- ²¹ J. Brandrup, E. H. Immergut, *Polymer Handbook*, Interscience Publishers, John Wiley, New York 1966, p. II-243
- ²² G. Smets, J. Roovers, W. van Humbeek, *J. Appl. Polym. Sci.* **5** (1961) 149